

# Compressible spherical dipolar glass model of relaxor ferroelectrics

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The interactions between the dielectric polarization and the fluctuations of the strain (stress) tensor in relaxor ferroelectrics are shown to give rise to the anisotropy of the anharmonic  $P^4$ -term in the Landau-type free energy, however, the harmonic  $P^2$ -term is still properly described by the rigid spherical random bond-random field model. These are the essential features of the compressible spherical dipolar glass model, which is used to calculate the singularities of the specific heat near field-induced critical points. The results agree with recent high-resolution calorimetric experiments in PMN [110].

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## I. INTRODUCTION

Relaxor ferroelectrics (relaxors) exhibit a variety of physical properties which are interesting for numerous practical applications, such as tunable capacitors, ultrasonic transducers, actuators, and pyroelectric detectors [1]. Sometimes relaxors are regarded as a subgroup of incipient ferroelectrics in view of the fact that they do not possess a polarized long-range ordered phase in zero applied electric field. However, in contrast to normal incipient ferroelectrics, relaxors undergo a freezing transition into a nonergodic glass-like phase below the so-called freezing temperature. If the relaxor is slowly cooled in a nonzero electric field  $E$ , it will pass through a sequence of quasi-stationary states. Thus, in order to stay close to thermal equilibrium, the experimental scale should increase steadily as the temperature is lowered. The corresponding  $E$ - $T$  phase diagram is shown in Fig. 1 for the case of  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN) in a field along the [110] direction [2]. The solid line in Fig. 1 separates the field-cooled dipolar glass phase from the field-induced long-range correlated ferroelectric phase. Similarly, the dotted line represents the boundary between the ergodic paraelectric phase and the frozen-in nonergodic dipolar glass phase. On approaching this line from the right, the longest dielectric relaxation time  $\tau(E, T)$  diverges according to the Vogel-Fulcher law [3, 4], reflecting the random character of the relaxor state.

Dielectric experiments in PMN [111] [5, 6] have shown that there is no frequency dispersion of the dielectric susceptibility in the region above the solid line, indicating that the relaxation times are finite and the system is ergodic. The transitions across the solid line, indicated by the arrows, are all first order and are characterized by a jump in the polarization  $P = P(E, T)$ . As one moves towards higher temperatures, the size of the jump

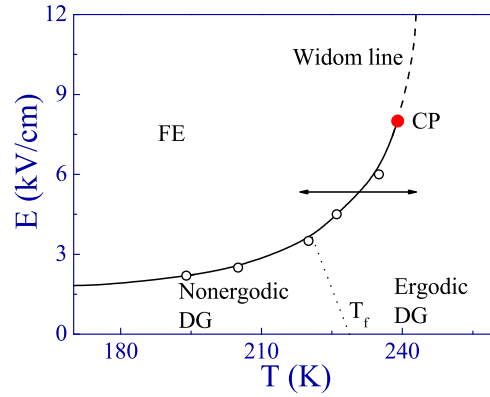


FIG. 1: Phase diagram for a relaxor with  $b < 0$ . The solid line separates the dipolar glass (DG) phase from the field-induced ferroelectric (FE) phase. The arrows indicate the direction of the field-cooling (-heating) process. Dashed line: Supercritical regime. Dotted line: Freezing line separating the ergodic dipolar glass phase from the nonergodic one. Open circles: Data from Ref. [2].

becomes smaller and finally disappears at a liquid-vapor-type critical point  $T_{CP}, E_{CP}$ , where the transition is second order [7]. Beyond this point, the relaxor is in a supercritical state characterized by a smooth evolution of  $P(E, T)$  and of the field-dependent dielectric susceptibility  $\chi(E, T) = (\partial P / \partial E)_T$ . The dashed line marks the positions of the maxima of  $\chi(E, T)$  (Widom line).

## II. POLARIZATION-STRESS COUPLING IN LANDAU FREE ENERGY

It had been suggested earlier [8] that when dealing with quasi-equilibrium states as in Fig. 1, the relaxor can be described in terms of a Landau theory based on the free energy density

$$F = F_0 + \frac{1}{2} a P^2 + \frac{1}{4} b P^4 + \frac{1}{6} c P^6 + \dots - EP. \quad (1)$$

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For simplicity we are dealing with a scalar order parameter  $P = P(E, T)$ , corresponding to the polarization vector along one of the symmetry directions in the crystal, i.e., [100], [110], or [111] in a system with average cubic symmetry. For an oblique direction of the electric field  $\vec{E}$  the quartic term should be written as

$$F_4 = \frac{1}{4} b_{ijkl} P_i P_j P_k P_l, \quad (2)$$

where the summation over all Cartesian indices is implied. Thus for a given symmetry direction,  $b$  will be a function of  $b_{ijkl}$ , which are components of a fourth rank tensor  $\mathbf{b}$ .

The first term  $F_0$  in Eq. (1) contains the contribution of all other degrees of freedom such as electrons, phonons, etc. The coefficient  $a = a(T)$  is related to the inverse quasistatic field-cooled susceptibility  $\chi_1$ , namely,  $a = (\varepsilon_0 \chi_1)^{-1}$ . The susceptibility  $\chi_1$  can be calculated from the static spherical random bond-random field (SRBRF) model of relaxor ferroelectrics [9, 10] and has the general form,

$$\chi_1 = \frac{\Theta(1-q)}{T - T_0(1-q)}, \quad (3)$$

which is well known from the theory of spin glasses and was found empirically to hold in the case of relaxors [11]. Here,  $\Theta$  is the Curie constant and  $T_0$  a measure of the average interaction between the elementary dipolar entities in the system. In relaxors, these are known to be the polar nanoregions (PNRs), which are formed below the Burns temperature [12]. Finally,  $q = q(T)$  is the dipolar glass order parameter, which is nonzero at all temperatures due to the presence of quenched random electric fields [13]. In zero applied field, the order parameter  $q$  is determined by the real solution of the following algebraic equation [9, 10]:

$$q = (J/kT)^2 (q + \Delta/J^2)(1-q)^2. \quad (4)$$

The parameter  $J$  is defined in terms of the variance  $J^2/N$  of the infinitely ranged random interactions of a spin-glass type, and  $\Delta$  the variance of local random fields. For PMN, the estimated values are  $J/k \sim 217$  K and  $\Delta/J^2 = 0.001$ , whereas  $T_0$  in Eq. (3) is of the order  $kT_0 \equiv J_0 \sim 0.9J$  [14].

The parameters  $b, c, \dots$  in Eq. (1) are related to the nonlinear susceptibilities  $\chi_3, \chi_5, \dots$ , which are defined as usual by the expansion  $P/\varepsilon_0 = P_s + \chi_1 E + \chi_3 E^3 + \chi_5 E^5 + \dots$ . In relaxors, the spontaneous polarization vanishes, thus by definition  $P_s \equiv 0$ , and the Landau coefficient  $b$  is given by  $b = -\chi_3/(\varepsilon_0^3 \chi_1^4)$ . It should be emphasized that in general both  $b$  and  $\chi_3$ , as well as higher order Landau coefficients in Eq. (1), depend on the direction of the field  $\vec{E}$  due to the anisotropy term (2).

The SRBRF model was originally introduced for an ideal isotropic relaxor system [9] in a *rigid* environment. Thus the nonlinear susceptibility  $\chi_3$  derived from it is

independent of the orientation and  $\chi_3^{rigid} < 0$ . Consequently,  $b_{rigid} > 0$ , i.e.,  $b_{rigid}$  is a positive scalar. Experiments on various relaxors have shown that  $\chi_3$  can either be positive or negative, depending on the particular system studied and on the field orientation [6, 15].

In order to derive a more general version of the model capable of reproducing the observed anisotropy of the coefficient  $b$ , we introduce a coupling between the polarization  $P$  and the strain tensor  $u_{ij}$  (or the *internal* stress tensor  $X_{ij}$ ). This suggests that we should consider the stress dependence of the Landau coefficients in Eq. (1). Focusing on the  $P^2$ -term, we first introduce a generalized Landau coefficient  $a_{kl} = \varepsilon_0^{-1}(\chi_1^{-1})_{kl}$ . Next, by expanding  $a(X_{ij}, T)_{kl}$  to linear order in  $X_{ij}$ , we replace the  $P^2$ -term in  $F$  by

$$\frac{1}{2\varepsilon_0} \left[ \chi_1^{-1} \delta_{kl} + \left( \frac{\partial(\chi_1^{-1})_{kl}}{\partial X_{ij}} \right)_{E,T} X_{ij} + \dots \right] P_k P_l. \quad (5)$$

The partial derivative is related to the electrostriction tensor  $Q_{ijkl}$ , namely, [16]

$$Q_{ijkl} = \frac{1}{2\varepsilon_0} \left( \frac{\partial(\chi_1^{-1})_{kl}}{\partial X_{ij}} \right)_{E,T}. \quad (6)$$

By adding the elastic energy, the free energy  $F$  acquires an additional term, which can be written as

$$F_X = \mathbf{X} \cdot \mathbf{Q} \cdot \mathbf{P}^2 + \frac{1}{2} \mathbf{X} \cdot \mathbf{C}^{-1} \cdot \mathbf{X}. \quad (7)$$

Here,  $\mathbf{C}$  is the elastic constant tensor and  $(\mathbf{P}^2)_{ij} = P_i P_j$ .

Minimizing  $F_X$  with respect to  $X_{ij}$  at constant temperature and field, we formally recover the free energy (1), however, the quartic term is now replaced by the general expression (2) with

$$b_{ijkl} = b_{rigid} \delta_{ij} \delta_{kl} + B_{ijkl}, \quad (8)$$

where the fourth rank tensor  $\mathbf{B}$  is given by

$$\mathbf{B} = -2\mathbf{Q} \cdot \mathbf{C} \cdot \mathbf{Q}. \quad (9)$$

In relaxors, the electrostriction effect is usually large and the magnitude of the tensor components  $B_{ijkl}$  may exceed the value of  $b_{rigid}$ . Obviously, the sign of  $B_{ijkl}$  will in general depend on the balance between the individual components of  $Q_{ijkl}$  and  $C_{ijkl}$ . Thus the resulting value of  $b$  for a symmetry direction can either be positive or negative.

The generalized Landau free energy (1) with  $a(T)$  given by the SRBRF model and the  $P^4$ -term having the form (2), and with quartic coefficients (8) given by Eq. (8), will be referred to as the Compressible Spherical Dipolar Glass (CSDG) Model.

We can evaluate the coefficients  $B_{ijkl}$  for the cases where values of  $Q_{ijkl}$  and  $C_{ijkl}$  are explicitly known. In Table I, these are listed for the PMN crystal using the Voigt notation, i.e.,  $B_{1111} = B_{11}$ , etc. The

TABLE I: Values of  $C_{ij}$  and  $Q_{ij}$  used to calculate  $B_{ij}$  from Eq. (9) and  $B^{[p]}$  from Eq. (10).

$C_{11}$	155.3 <sup>a,b</sup>	$C_{12}$	78.4 <sup>a</sup>	$C_{44}$	68.3 <sup>a,b</sup>	[GPa]
$Q_{11}$	2.52 <sup>c</sup>	$Q_{12}$	-0.96 <sup>c</sup>	$Q_{44}$	6.96 <sup>d</sup>	[10 <sup>-2</sup> m <sup>4</sup> C <sup>2</sup> ]
$B_{11}$	0.141	$B_{12}$	0.483	$B_{44}$	-1.654	[10 <sup>8</sup> Vm <sup>5</sup> C <sup>3</sup> ]
$B^{[100]}$	0.141	$B^{[110]}$	-0.84	$B^{[111]}$	-1.836	[10 <sup>8</sup> Vm <sup>5</sup> C <sup>3</sup> ]

<sup>a</sup>Reference [18]; <sup>b</sup>Reference [19]; <sup>c</sup>References [16, 17]; <sup>d</sup>estimated [17]

value of  $Q_{44}$  can be estimated from the relation [17]  $Q_{44} = (Q_{11} - Q_{12})/2$ . From Eq. (9) we can then calculate the coefficients  $B_{11}$ ,  $B_{12}$ , and  $B_{44}$  (see Table I). For a symmetry direction  $p$ , where  $p$  refers to [100], [110], or [111], the Landau coefficient  $b = b^{[p]}$  in Eq. (1) can be expressed in terms of  $b_{ij}$  as follows:

$$b^{[100]} = b_{11}; \quad (10a)$$

$$b^{[110]} = \frac{1}{2}(b_{11} + b_{12} + 2b_{44}); \quad (10b)$$

$$b^{[111]} = \frac{1}{3}(b_{11} + 2b_{12} + 4b_{44}). \quad (10c)$$

We can now write  $b^{[p]} = b_{rigid}^{[p]} + B^{[p]}$ , where  $b_{rigid} > 0$ . Thus the rigid model always yields an isotropic, positive contribution to  $b^{[p]}$ , however, the new term  $B^{[p]}$  is in general anisotropic. The corresponding values of  $B^{[p]}$  for PMN are listed in Table I. While  $B^{[100]} > 0$ , we can see that  $B^{[110]}$  and  $B^{[111]}$  are both negative. Thus,  $b^{[100]} > 0$  and  $\chi_3^{[100]} < 0$ . On the other hand, if  $|B^{[p]}| > b_{rigid}$  for  $p = [110]$  and  $[111]$ , the values of  $b^{[110]}$  and  $b^{[111]}$  will be negative, implying  $\chi_3^{[110]} > 0$  and  $\chi_3^{[111]} > 0$ , respectively. It is interesting to note that Tagantsev and Glazounov [15] observed  $\chi_3^{[111]} > 0$ , but  $\chi_3^{[100]} < 0$  in PMN, in agreement with the above conclusions. Quasistatic measurements of polarization versus field along [111] and [100] directions also agree with these results [6]. As shown below, the sign of  $b^{[p]}$  has important consequences for the existence of field-induced critical points for fields along the direction  $[p]$ .

### III. FIELD INDUCED CRITICAL POINTS

The temperature and field dependence of the dielectric polarization during a field-cooled (or field-heated) quasi-stationary process is calculated by minimizing numerically the free energy (1). This procedure automatically selects the correct solution of the minimization condition  $(\partial F / \partial P)_{E,T} = 0$ . The parameter  $a = a(E, T)$  is calculated from the SRBRF model [8], while  $b$  and  $c$  are treated as free parameters. To ensure stability, we assume that  $c > 0$  and consider two cases,  $b > 0$  and  $b < 0$ . For  $b > 0$ ,  $P(E, T)$  is found to increase monotonically with  $E$  and decrease with  $T$ , and no critical singularities of the susceptibility can be expected. For  $b < 0$ , however,  $P(E)$  makes a discontinuous jump at some value of  $E$  at low temperatures. As  $T$  increases, the jump becomes smaller and finally disappears at the critical point

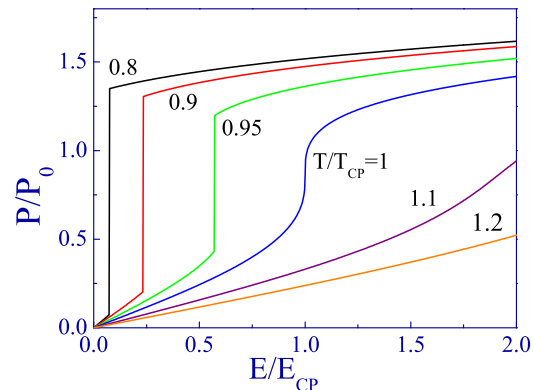


FIG. 2: Field dependence of  $P(E)$  for a relaxor with  $b < 0$  and several values of temperature  $T$  close to the critical temperature  $T_{CP}$ , obtained by minimizing the free energy (1). Note that these calculations are only valid in the ergodic region above the freezing line shown in Fig. 1.

$E_{CP}, T_{CP}$ , where the slope of  $P(E)$  is infinite. This is illustrated in Fig. 2 for  $b = -0.2$  and  $c = 0.08$ , corresponding to PMN [110]. A similar behavior of  $P(T)$  had been obtained earlier for PMN [111], where  $b = -1/3$  and  $c = |b|$  [8].

The coordinates of the critical point are determined from the relations [8, 20]

$$a(T_{CP}) = \frac{9b^2}{20c}; \quad E_{CP} = \frac{6b^2}{25c}P_{CP}, \quad (11)$$

where  $P_{CP} = \sqrt{-3b/(10c)}$  is the polarization at the critical point. The critical exponents at the field-induced critical point differ from the usual mean field exponents for ferroelectrics in zero field [8].

The  $E$ - $T$  phase diagram for PMN corresponding to cooling in a field along the [110] direction is plotted in Fig. 1 using the data points from Ref. [2]. Similar phase diagrams were obtained earlier for PMN [100] and [111] [6, 21]. For  $E \parallel [100]$  no critical point was found, but the phase diagram for the [111] direction was shown to be analogous to the [110] case, in agreement with the above estimates for  $b^{[p]}$ . A similar conclusion had been reached earlier by Zhao et al. [22].

The existence of field-induced phase transitions and critical points has recently been confirmed in PMN [110]

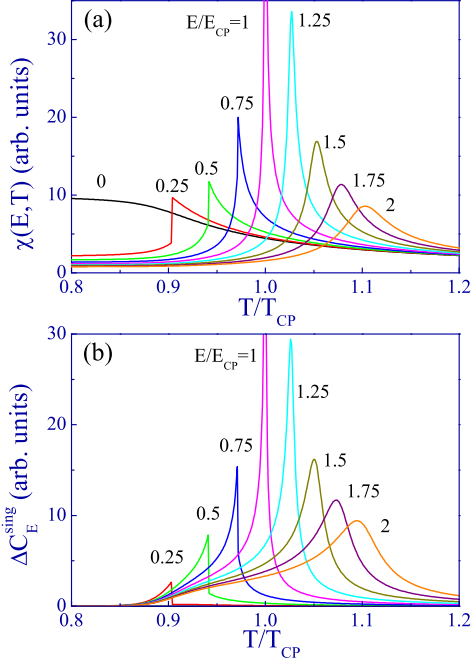


FIG. 3: (a) Calculated temperature dependence of the susceptibility  $\chi(E, T)$  for a set of field values  $E/E_{CP}$ , as indicated. (b) Same, but for the singular part of the specific heat from Eq. (16).

by measuring the specific heat using high-resolution calorimetry [2]. The excess specific heat  $\Delta C_E(T)$ , which is due to the contribution of the dipolar degrees of freedom, namely, PNRs can be derived from the free energy Eq. (1) by applying the thermodynamic relation for the entropy  $S = -(\partial F/\partial T)_E$ . We can write  $S = S_0 + S_{dip}$ , where  $S_0 = -(\partial F_0/\partial T)_E$  and the dipolar part  $S_{dip}$  is defined as the contribution of all  $P$ -dependent terms in Eq. (1),

$$S_{dip} = - \left( \frac{1}{2} a_1 P^2 + \frac{1}{4} b_1 P^4 + \frac{1}{6} c_1 P^6 + \dots \right), \quad (12)$$

where  $a_1 \equiv da/dT$ ,  $b_1 \equiv db/dT$ , etc., and the condition  $(\partial F/\partial P)_E = 0$  has been applied [8]. The dipolar excess specific heat capacity at constant field is given by  $\Delta C_E = T(\partial S_{dip}/\partial T)_E$ , and at constant polarization similarly by  $\Delta C_P = T(\partial S_{dip}/\partial T)_P$ . These two quantities are related by the standard thermodynamic relation

$$\Delta C_E = \Delta C_P + T\chi(E, T)[(\partial E/\partial T)_P]^2, \quad (13)$$

where  $\chi(E, T) = (\partial P(E, T)/\partial E)_T$  is the field-dependent susceptibility. The partial derivative in Eq. (13) can be evaluated from the equation of state  $E = aP + bP^3 + cP^5 + \dots$ , i.e.,

$$(\partial E/\partial T)_P = a_1 P + b_1 P^3 + c_1 P^5 + \dots \quad (14)$$

To calculate the expression on the right hand side we would, therefore, need to know the temperature dependence of the coefficients  $a, b, c$ , etc. In practice,  $a(T)$

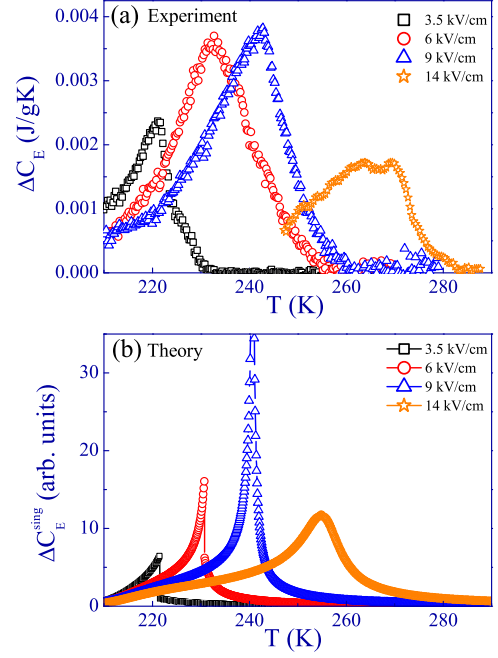


FIG. 4: (a) Experimental data showing the specific heat anomalies occurring in PMN [110] for four selected values of the electric field, obtained by high-resolution calorimetry [2]. (b) Calculated temperature dependence of the singular part of the excess specific heat  $C_E^{sing}$  for a relaxor with  $b = -0.2$  and  $c = 0.08$  and the same field values as used in the experiment. The remaining parameters are taken from Ref. [8].

is known from the SRBRF model through the relation  $a = (\epsilon_0 \chi_1)^{-1}$ , and  $a_1(T)$  follows from the temperature derivative of  $\chi_1(T)$ . On the other hand,  $b(T)$  and  $c(T)$  could, in principle, be estimated from the nonlinear susceptibilities as given by the SRBRF model and the  $\mathbf{Q}$  and  $\mathbf{C}$  tensors. In the following we will simply assume that  $b$  and  $c$  are effectively constant in the temperature range of interest, and thus  $b_1$  and  $c_1$  will be neglected.

The calculated temperature dependence of  $\chi(E, T)$  is shown in Fig. 3a for a set of values  $0 \leq E \leq 2E_{CP}$ . Here we used the parameter values of  $J$ ,  $J_0$ , and  $\Delta$  determined earlier from the dielectric data [14], and the remaining parameters were chosen as  $b = -0.2$  and  $c = 0.08$ . At  $E = 0$ , the zero-field cooled susceptibility  $\chi_1$  is recovered. For  $0 < E \leq E_{CP}$ ,  $\chi(E, T)$  exhibits a jump at the first order transitions and diverges at the critical point. For  $E > E_{CP}$ , however,  $\chi(E, T)$  is characterized by rounded maxima, in accordance with the smooth behavior of  $P(E, T)$  in the supercritical regime.

The first term in Eq. (13) is readily shown to be

$$\Delta C_P = -T \left( \frac{1}{2} a_2 P + \frac{1}{4} b_2 P^3 + \frac{1}{4} c_2 P^5 + \dots \right), \quad (15)$$

where  $a_2 \equiv da_1/dT$  etc. Again, the corresponding derivatives of  $b, c, \dots$  are not known, and we will neglect them. The quantity  $a_2$  can, however, be calculated from  $a(T)$ .

It shows a sharp peak around the static "freezing" temperature  $T_f = (J^2 + \Delta)^{1/2}/k$ , but is rather small elsewhere. We may conclude that  $\Delta C_P$  will be nonsingular for all values of  $E, T$ , however, its precise behavior could only be determined if the values of  $b(T)$  and  $c(T)$  were known.

The temperature dependence of the singular part of  $\Delta C_E(T)$  can be calculated from Eqs. (13) and (14), namely,

$$\Delta C_E^{sing} \cong T\chi(E, T)(a_1 P)^2, \quad (16)$$

and is displayed in Fig. 3b for the same set of parameters as in Fig. 3a. The positions of the singularities of  $\Delta C_E^{sing}(T)$  coincide with those of  $\chi(E, T)$ , however, the direction of the jumps is reversed due to the last factor in Eq. (16).

The experimental data for  $\Delta C_E(T)$  in PMN [110] obtained by high-resolution calorimetry [2] are shown in Fig. 4a for four discrete values of the electric field  $E$ . For comparison, the theoretical prediction for the singular part of  $\Delta C_E(T)$ , calculated from Eq. (16) at the same field values, is plotted in Fig. 4b. The experimental values for the critical field and the critical temperature are given by  $E_{CP} \cong 8$  kV/cm and  $T_{CP} \cong 240$  K, respectively [2].

The predicted behavior of  $\Delta C_E^{sing}(T)$  qualitatively agrees with the experimental values of  $\Delta C_E(T)$ , however, the experimental anomalies appear to be broader

than the calculated ones. There are several reasons for this broadening, for example, finite size effects, structural inhomogeneities, and slow relaxation.

It should be stressed that at zero field ( $E = 0$ ), no anomalies in  $\Delta C_E(T)$  were found in the entire temperature range studied, in accordance with the CSDG model. This contrasts with the so-called random field scenario, according to which PMN [110] is assumed to undergo a ferroelectric phase transition at  $E = 0$ . This point has been discussed in more detail in Ref. [2].

#### IV. CONCLUSIONS

We have shown that the electrostrictive coupling between the dielectric polarization  $P$  and the strain or stress tensor fluctuations in a relaxor ferroelectric gives rise to an anisotropy of the  $P^4$ -term in the Landau free energy. For a given symmetry direction of the applied field the effective Landau coefficient  $b$  may become negative, thus leading to the field-induced critical points. The compressible spherical dipolar glass model predicts singularities of the dipolar specific heat near critical points, in agreement with high-resolution calorimetry experiments in PMN [110] [2].

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